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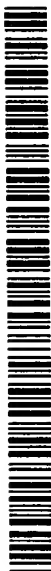


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(54) Title: BI-AXIALLY ORIENTED AND HEAT-SET MULTILAYER THERMOPLASTIC FILM FOR PACKAGING

(57) Abstract: A multi-layer, thermoplastic film bi-axially oriented at a stretching ratio \geq about 3.0:1 in the machine direction and at a stretching ratio \geq about 6.0:1 in the transverse direction, which film comprises a layer a) comprising at least 50 wt. % of a crystalline or partially crystalline co-polyamide characterized by a $T_g \leq 100^\circ\text{C}$, and at least one outer heat-sealing layer b) comprising a polyolefin, said film being further characterized in that it has a % free shrink at $100^\circ\text{C} \leq 3$ in each direction.

BI-AXIALLY ORIENTED AND HEAT-SET MULTILAYER THERMOPLASTIC FILM FOR PACKAGING

The present invention refers to a highly oriented, heat-set, multilayer thermoplastic
5 film comprising a layer comprising a polyamide, and an outer heat-sealing layer comprising a polyolefin, to a process for the manufacture thereof and to the use of the film as a packaging material.

Multi-layer thermoplastic films are typically employed for the packaging of food and non-food products.

10 One method for the packaging of products by means of a flexible thermoplastic film provides for the use of pre-made bags or pouches of the suitable size, where the product to be packaged is loaded either manually or automatically. The loaded bags or pouches are optionally vacuumized, and/or gas-flushed and then their open mouth is clipped or sealed.

15 Another method is by means of a form-fill-seal machine, such as a Horizontal Form-Fill-Seal (HFFS) or a Vertical Form-Fill-Seal (VFFS) machine. A FFS machine, either Horizontal or Vertical, typically includes a former for forming a flat web of flexible film into a tubular configuration, a longitudinal sealer to seal the longitudinal edges of the film in the tubular configuration, either by means of a lap seal or a fin seal, a
20 conveyor for feeding the products into the tubular film one after the other in suitably spaced configuration, or a feeding tube in case of a VFFS machine, and a transverse sealer for sealing the tubular film in a cross-wise direction to separate the products into discrete packages.

A third method involves the use of shaped containers of widely varying
25 configurations and materials, such as trays, closed by flat lids sealed to the containers' flanges.

Because of the commercial use, the nature of the packaging process and the conditions the packages are subjected to during the storage and distribution cycles,

films for these types of applications need to have an optimum balance of performance properties, including

- good mechanical properties, in particular high modulus to provide a satisfactory machinability of the film mainly in high speed packaging processes and at the same time good puncture resistance to guarantee protection of the packaged product from the intrusion of unwanted materials such as dust and dirt,
- good heat-sealability properties, in particular low temperature heat-sealability combined with strong seal strength particularly when the film is sealed to itself,
- good optical properties, in particular low haze and high gloss,
- no shrinkage even at high temperatures, as in some of these application hot products are packaged, and, often,
- oxygen barrier properties.

The packaging materials currently used for these types of applications are cast coextruded sheets of high thickness containing polyolefin outer layers and as an internal oxygen barrier layer either a polyamide and/or an ethylene-vinyl alcohol layer. In order to achieve the desired mechanical properties, the thickness of these cast coextruded structures is fairly high and sheets of a thickness ranging from at least 60 to about 250 μm are typically employed depending on the specific application. Alternatively, laminates of a biaxially oriented and heat-set resin (such as BO-PET, BO-PP, or BO-PA) glue laminated to a heat-sealing and optionally barrier film are employed. In this latter case the thickness required may be lower as the presence of an oriented layer improves the mechanical properties of the film. Laminates having a thickness of from about 40 to about 100 μm are in fact generally available for these applications. The lamination is however an additional step in the manufacturing process that adds to the cost of the end products so that for economy reasons very often the thicker cast co-extruded structures are preferred.

It has now been found that it is possible to obtain a film that has the desired balance of properties, including good mechanical properties, at a very low thickness with a manufacturing process that does not require any lamination step.

It has been found in fact that it is possible to orient a structure having at least an
5 outer heat-sealing polyolefin layer and a polyamide layer, at very high stretching ratios by suitably selecting the polyamide among the co-polyamides having a $T_g \leq 100^\circ\text{C}$ and that the orientation with such high stretching ratios give to the film remarkable mechanical and oxygen barrier properties.

Orientation is a process whereby a plastic film or sheet is stretched in such a way to
10 orient the polymeric chains of the plastic material in the direction of the force applied. Orientation is known to increase the strength and stiffness of the polymer system, and therefore the tensile properties of the film.

Polyamides are widely employed in the manufacture of oriented films.

They can be employed i.a. as core layers of multi-layer films having a heat-sealable
15 polyolefin layer, because of their gas-barrier properties. It is in fact possible to modulate the gas permeability of the end films by suitably selecting the type of polyamide of the core layer.

In general, oriented films comprising a polyamide layer and an outer heat-sealing polyolefin layer, are obtained by a tubular orientation process. In said process a thick
20 multi-layer tube is first extruded through a round die, quenched as rapidly as possible to prevent or slow down crystallization, reheated, e.g. by passing it into a hot water bath and/or an IR or hot air oven, and then stretched in the transverse direction (TD) by introducing into the tube an air pressure that expands the tube diameter to a sort of a bubble and in the machine direction (MD) by running the two sets of nip rolls that
25 contain said bubble at a different speed.

The orientation ratios that can be applied with the tubular orientation processes are however limited and ratios up to about 3.5:1 are typically applied.

Higher stretching ratios could, in line of principle, be employed using flat extrusion and flat stretching. Flat stretching may be done sequentially, i.e. the extruded tape is first stretched in the MD and then in the TD, or simultaneously. In the sequential flat stretching the MD stretching is accomplished by drawing the heated sheet between sets
5 of heated rolls with the downstream set moving at a higher speed and the TD stretching is obtained by means of a tenter frame, a machine that consists of two continuous chains on which are mounted clamps gripping the two edges of the film and carrying it along as the chain is driven forward. In the simultaneous stretching the extruded cast sheet is fed to a pre-heating zone of the simultaneous tenter apparatus, where the film is
10 clipped but not stretched yet, and brought to the temperature desired for bi-axial orientation and then simultaneously stretched in the machine and the transverse direction.

In case of mono-layer structures where the orientation temperature specific for the resin employed, can be applied, stretching ratios for the flat, tenter frame orientation process are up to about 7:1 in MD and up to about 12:1 in TD.

15 In the patent literature there are described oriented films comprising a polyamide layer and a polyolefin outer layer obtained by tenter frame stretching, that however have been stretched to a limited stretching ratio ($< 2.2:1$ in MD and $> 4:1$ in TD in Japanese kokai 79/15981 (Derwent AN 79-20793B) or $3:1$ in MD and $4:1$ in TD in Japanese kokai 92/52137 (Derwent AN 92-117943)).

20 The use of high stretching temperatures, particularly for the transverse stretching, would help to increase the stretching ratios but these high temperatures would not be compatible with the presence of the polyolefin resin of the outer layer.

It has now been found that it is possible to obtain a multi-layer film comprising a layer comprising a polyamide and an outer heat-sealing layer comprising a polyolefin,
25 which film has been oriented at a stretching ratio \geq about $3.0:1$ in the machine direction and at a stretching ratio \geq about $6.0:1$ in the transverse direction, when the polyamide is a crystalline or partially crystalline *co*-polyamide with a $T_g \leq 100$ °C.

It has been found that if a heat-setting step follows the bi-axial stretching, the highly oriented multi-layer film, thus obtained, is characterized by the following combination of properties that would render it particularly suitable for the above indicated packaging applications :

- 5 - good mechanical properties, in particular a very high puncture resistance, comparable to that of much thicker cast coextruded films still containing polyamides,
- good heat-sealability,
- good optical properties,
- 10 - from good to very good oxygen barrier properties depending on the particular copolyamide employed, and
- no shrinkage at high temperatures ($\leq 3\%$ at $100\text{ }^{\circ}\text{C}$ in each direction).

An object of the present invention is therefore a multi-layer, thermoplastic film oriented at a stretching ratio \geq about 3.0:1 in the machine direction and at a stretching
15 ratio \geq about 6.0:1 in the transverse direction, which film comprises
 a layer a) comprising at least 50 wt. % of a crystalline or partially crystalline *co*-polyamide characterized by a $T_g \leq 100\text{ }^{\circ}\text{C}$, and
 at least one outer heat-sealing layer b) comprising a polyolefin,
 said film being further characterized in that it has a % free shrink at $100\text{ }^{\circ}\text{C} \leq 3$ in
20 each direction.

Another object of the present invention is a process for the manufacture of such a film which process comprises stretching an extruded tape comprising
 a layer a) comprising at least 50 wt. % of a crystalline or partially crystalline *co*-polyamide characterized by a $T_g \leq 100\text{ }^{\circ}\text{C}$, and
25 at least one outer heat-sealing layer b) comprising a polyolefin,
 in the machine direction with a stretching ratio of $\geq 3.0:1$ and in the transverse direction with a stretching ratio of $\geq 6.0:1$, either sequentially or simultaneously, at

suitably selected orientation temperatures and then heat-setting the film at a temperature from about 15 °C below the orientation temperature to the orientation temperature applied or even higher.

DEFINITIONS

5 As used herein, the term "film" is used in a generic sense to include a plastic flexible web, regardless of whether it is a film or a sheet. Preferably, films of use in the present invention have a thickness of 100 µm or less, more preferably they have a thickness of from about 10 to about 90 µm, and even more preferably of from about 12 to about 80 µm.

10 The term "oriented" designates a structure which has been stretched at a temperature - indicated as the "orientation temperature" - higher than the T_g of each of the resins making up the structure and lower than the m.p. of at least one of said resins. As used herein the term "oriented" designates bi-axially oriented materials, i.e. materials wherein the stretching is carried out in two perpendicular directions, i.e. the machine or
15 longitudinal direction (MD) as well as the transverse direction (TD).

As used herein, the term "*homo*-polymer" is used with reference to a polymer resulting from the polymerization of a single monomer, i.e., a polymer consisting essentially of a single type of repeating unit.

As used herein, the term "*co*-polymer" refers to polymers formed by the
20 polymerization reaction of at least two different monomers.

As used herein, the term "polymer" refers to both *homo*-polymers and *co*-polymers as defined above.

In particular the term "polyamide", as used herein, refers to both polyamide *homo*-polymers and polyamide *co*-polymers, also called *co*-polyamides.

25 As used herein the term "*co*-polyamide" on the other hand identifies the polyamide product built from at least two different starting materials, i.e. lactams, aminocarboxylic acids, equimolar amounts of diamines and dicarboxylic acids, in any

proportion; this term therefore also encompasses *ter*-polyamides and, in general, *multi*-polyamides.

As used herein, the term "polyolefin" refers to any polymerised olefin, which can be linear, branched, cyclic, aromatic, substituted, or unsubstituted. More specifically, included in the term polyolefin are *homo*-polymers of olefin, *co*-polymers of olefin, *co*-polymers of an olefin and a non-olefinic comonomer copolymerizable with the olefin, such as vinyl monomers, modified polymers thereof, and the like. Specific examples include ethylene *homo*-polymers, ethylene- α -olefin copolymers and terpolymers, propylene *homo*-polymers, propylene- α -olefin copolymers and terpolymers, butene *homo*-polymers, butene- α -olefin copolymers, ethylene-vinyl acetate copolymers, ethylene-ethyl acrylate copolymers, ethylene-butyl acrylate copolymers, ethylene-methyl acrylate copolymers, ionomer resins, and modified polyolefins.

As used herein the term "ethylene *homo*-polymers", "propylene *homo*-polymers", or "butene *homo*-polymers" identify polymers consisting essentially of an ethylene, propylene or butene repeating unit respectively.

As used herein, the phrase "ethylene α -olefin *co*-polymer" as well as the phrase "ethylene α -olefin *ter*-polymer" refers to such heterogeneous materials as linear low density polyethylene (LLDPE), linear medium density polyethylene (LMDPE) and very low and ultra low density polyethylene (VLDPE and ULDPE); and homogeneous polymers such as metallocene catalyzed polymers such as for instance EXACT™ materials supplied by Exxon, AFFINITY™ and ENGAGE™ materials supplied by Dow, LUFLEXEN™ materials supplied by BASF and TAFMER™ materials supplied by Mitsui Petrochemical Corporation. These materials generally include *co*-polymers of ethylene with one or more *co*-monomers selected from C₄ to C₁₀ α -olefins such as butene-1 (i.e., 1-butene), hexene-1, octene-1, etc.

As used herein, the phrase "modified polyolefin", as well as more specific phrases such as "modified ethylene vinyl acetate *co*-polymer", or "modified ethylene- α -olefin

co-polymer" refer to such polymers having an acid or, preferably, an anhydride functionality, such as maleic or fumaric acid, or anhydride, grafted thereon and/or *co*-polymerized therewith and/or blended therewith. Preferably, such modified polymers have the anhydride functionality grafted on or polymerized therewith, as opposed to
5 merely blended therewith.

As used herein, the phrase "directly adhered", as applied to film layers, is defined as adhesion of the subject film layer to the object film layer, without a tie layer, adhesive, or other layer there-between. In contrast, as used herein, the word "between", as applied to a film layer expressed as being between two other specified layers, includes
10 both direct adherence of the subject layer to the two other layers it is between, as well as lack of direct adherence to either or both of the two other layers the subject layer is between, i.e., one or more additional layers can be imposed between the subject layer and one or more of the layers the subject layer is between.

As used herein, the phrases "inner layer" and "internal layer" refer to any film layer
15 having both of its principal surfaces directly adhered to another layer of the film.

As used herein, the phrase "outer layer" refers to any film layer having only one of its principal surfaces directly adhered to another layer of the film.

As used herein, the term "core", and the phrase "core layer" refer to any internal film layer that has a primary function other than serving as an adhesive or compatibilizer for
20 adhering two layers to one another.

The term "barrier" as used herein means a layer of a multilayer film that comprises a material which acts as a physical barrier to gaseous oxygen molecules. Typically the presence of the polyamide barrier layer in the film of the present invention will reduce the oxygen permeability of the film to less than $700 \text{ cm}^3/\text{m}^2 \cdot \text{day} \cdot \text{bar}$, at 23°C and 0 %
25 relative humidity. The oxygen permeability value is obtained in accordance with ASTM D3985-81.

Additional "barrier layers" may be present, such as layers comprising PVDC,

ethylene-vinyl alcohol *co*-polymers, polyamides, blends of ethylene-vinyl alcohol *co*-polymers and polyamides, etc.

As used herein, the term "PVDC" refers to a vinylidene chloride copolymer wherein a major amount of the copolymer comprises vinylidene chloride and a minor amount of the copolymer comprises one or more unsaturated monomers copolymerisable therewith, typically vinyl chloride, and alkyl acrylates or methacrylates (e.g. methyl acrylate or methacrylate) or to a blend thereof in different proportions. Generally said PVDC contains plasticizers and/or stabilizers as known in the art.

As used herein, the phrase "bulk layer" refers to any layer that is present for the purpose of improving the abuse-resistance, toughness, modulus, etc., of the film. Bulk layers generally comprise polymers which are inexpensive relative to other polymers in the film which provide some specific purpose unrelated to abuse-resistance, modulus, etc.

As used herein, the phrase "tie layer" refers to any internal layer having the primary purpose of adhering two layers to one another.

As used herein the sentence "crystalline or at least partially crystalline *co*-polyamide" is used to distinguish the *co*-polyamide referred to from the amorphous ones, wherein the amorphous polyamides are characterized by no measurable melting point (and correspondingly by a heat of fusion less than 2.1 J/g), when measured by DSC according to ASTM 3417.

As used herein the term "polyester" is intended to refer to any thermoplastic film-forming, polyester and *co*-polyester comprising alkylene terephthalate or alkylene naphthalenate as the main recurring units in the polymer chain.

Polyesters comprising alkylene terephthalate as the main recurring units in the polymer chain are however preferred. These polyesters are produced mainly by the polycondensation of terephthalic acid or an ester-forming derivative thereof with an alkylene dihydroxyl compound. Examples of the alkylene dihydroxyl compounds

include ethylene glycol, propylene glycol, butanediol, neopentyl glycol and the ester-forming derivatives thereof.

The copolyesters will comprise these polyalkylene terephthalate groups as the main constituent units and 30 % molar or less, preferably 20 % molar or less of another
5 comonomer. Examples of the comonomers that can be used are dicarboxylic acids such as isophthalic, naphthalendicarboxylic, cyclohexanedicarboxylic, adipic, and sebacic acids as well as the substituted derivatives thereof. These dicarboxylic acids can be used in the form of ester-forming derivatives such as lower alcohol esters. Examples of the dihydroxyl compounds for forming the copolyesters include one or more of
10 hydroquinone, dihydroxyphenyl, cyclohexanediol, polyoxyalkylene glycols and the substituted derivatives thereof.

DETAILED DESCRIPTION OF THE INVENTION

A first object of the present invention is a multi-layer, thermoplastic film oriented at a stretching ratio \geq about 3.0:1 in the machine direction and at a stretching ratio \geq
15 about 6.0:1 in the transverse direction, which film comprises

a layer a) comprising at least 50 wt. % of a crystalline or partially crystalline *co*-polyamide characterized by a $T_g \leq 100$ °C, and

at least one outer heat-sealing layer b) comprising a polyolefin,

said film being further characterized in that it has a % free shrink at 100 °C ≤ 3 in
20 each direction.

In a preferred embodiment of the present invention, the film is oriented at a stretching ratio \geq about 3.5:1, more preferably \geq about 3.8:1, and even more preferably \geq about 4.0:1, in the machine direction and at a stretching ratio \geq about 6.2:1, and more preferably \geq about 6.5:1, in the transverse direction.

25 Examples of crystalline or partially crystalline *co*-polyamides characterized by a $T_g \leq 100$ °C that can suitably be employed in layer a), are certain polyamide aliphatic *co*-polymers obtained by *co*-polymerization of ϵ -caprolactam and ω -laurolactam

(polyamides 6/12 such as Grilon™ CF6S commercially available from EMS), certain aliphatic *co*-polymers obtained by *co*-polymerization of ϵ -caprolactam, hexamethylenediamine and azelaic acid (polyamides 6/69 such as Grilon™ CF62BS commercially available from EMS), polyamide *co*-polymers obtained from meta-xylylendiamine, adipic acid and isophthalic acid (MDX6/MDXI such as Grilon™ FE 4581 commercially available from EMS), some multi-polyamides obtained from hexamethylenediamine, meta-xylylendiamine, adipic acid, and sebacic acid (such as Grilon™ XE3569 commercially available from EMS).

The *co*-polyamides of layer a) can be used alone or admixed with any other resin compatible therewith provided they would not impair the orientability of the overall structure, such as less than about 50 wt. %, preferably less than about 40 wt. %, and even more preferably less than about 30 wt. % of amorphous polyamides, ethylene-vinyl alcohol *co*-polymers, polyesters, *co*-polyesters, or even crystalline or partially crystalline polyamides having a $T_g > 100^\circ\text{C}$, etc.

The thickness of the *co*-polyamide comprising layer a) is typically of from about 1.5 to about 25 μm . Layers thinner than 1.5 μm would not provide the film with the desired mechanical and barrier properties, while layers thicker than 25 μm would increase the cost of the film unnecessarily as the advantages brought by a further increase in the wt. % amount of *co*-polyamide in the overall film would not be dramatic. Preferably the thickness of the *co*-polyamide comprising layer a) is of from about 2.5 to about 15 μm , and more preferably of from about 3.0 to about 10 μm ,

In the films according to the present invention the outer heat-sealing layer b) may comprise a single polymer or a blend of two or more polymers as known in the art. Preferably the melting point of the polyolefin resin(s) of the outer heat-sealing layer b) will be $< 150^\circ\text{C}$, and preferably $< 140^\circ\text{C}$. In a more preferred embodiment it will be comprised between about 80°C and about 135°C and in an even more preferred embodiment it will be comprised between about 90°C and about 128°C .

Such a layer may for example comprise one or more heterogeneous or homogeneous ethylene- (C₄-C₈)- α -olefin *co*-polymers having a density ≤ 0.925 g/cm³; blends thereof with minor amount of polyethylene *homo*-polymers or heterogeneous or homogeneous ethylene- (C₄-C₈)- α -olefin *co*-polymers having a density > 0.925 g/cm³; ethylene-vinyl acetate *co*-polymers; ethylene-acrylic or methacrylic acid *co*-polymers including ionomers; blends of heterogeneous or homogeneous ethylene-(C₄-C₈)- α -olefin *co*-polymers having a density from about 0.915 g/cm³ to about 0.935 g/cm³ with ethylene-vinyl acetate *co*-polymers or ethylene-alkyl (meth)acrylate *co*-polymers; ethylene-propylene-*co*-polymers; ethylene-propylene-butene *ter*-polymers; ethylene-alkyl acrylate-maleic anhydride *ter*-polymers; and the like polymers.

In a preferred embodiment of the present invention the heat-sealing layer b) will comprise a heterogeneous or homogeneous ethylene-(C₄-C₈)- α -olefin *co*-polymer having a density ≤ 0.925 g/cm³, and even more preferably a heterogeneous or homogeneous ethylene-(C₄-C₈)- α -olefin *co*-polymer having a density comprised between about 0.900 g/cm³ and about 0.922 g/cm³. The Melt Index of said heterogeneous or homogeneous ethylene-(C₄-C₈)- α -olefin *co*-polymer may range from about 0.1 to about 15 g/10' (measured by ASTM D-1238, Condition E). However, preferred values are in the range 0.5-10 g/10' and still more preferred values are in the range 1.0-7.0 g/10'.

The thickness of the outer heat-sealing b) is generally higher than 2 μ m, and preferably higher than 3 μ m.

In certain cases, depending on the polyolefin used for the outer heat-sealing layer b), it may be necessary or advisable to position a tie layer c) between the layer comprising the *co*-polyamide and the outer heat-sealing polyolefin one, in order to get a sufficient bond between the film layers. Preferred resins for such a tie layer will be e.g. modified ethylene- α -olefin *co*-polymers or modified *co*-polymers of ethylene and an ethylenically unsaturated ester, typically modified ethylene-vinyl acetate *co*-polymers.

In a preferred embodiment of the present invention the *co*-polyamide layer a) is an internal layer and the film has an additional outer layer d).

Said second outer layer d) may comprise one or more polyolefins, modified polyolefins, polyamides, and polyesters.

5 The thickness of said outer layer d) is not a critical feature and the optimized value will depend on the overall thickness of the structure, the type of resin employed therefor, and the function said outer layer d) would serve. Typically said outer layer d) will have a thickness comprised between about 1 and about 30 μm .

10 In a preferred embodiment of the invention said outer layer d) will comprise a polyolefin.

Preferably, but not necessarily, in such a case the composition of the outer layer d) will be the same of the outer heat-sealing layer b), so as to provide for a symmetrical structure.

15 The use of a symmetrical structure is highly preferred when thin films (from about 10 to about 40 μm) are desired to be employed in high-speed HFFS (Horizontal-Form-Fill-Seal) machines. A symmetrical structure does not give any curl and if the modulus is sufficiently high has a good machinability. Furthermore, a symmetrical structure can also be lap-sealed, if desired, still giving strong seals.

20 In some cases however, for instance when the film has to be used in the manufacture of pouches that need to be easily openable, the composition of the second outer layer d) may be different from that of the layer b) and for example it may comprise a so-called "peelable" blend as known in the art. In such a case it would in fact be possible to manufacture a pouch, such as by means of a HFFS or VFFS machine, wherein the transverse fin seals will be very strong seals and the longitudinal lap seal will be a
25 peelable one. This will provide for the integrity of the package during conventional storage and handling conditions and easy openability, when desired, by a peeling mechanism.

Alternatively, when an easy opening pouch is desired, the outer layer d) may comprise a blend of at least two thermoplastic polymers known to provide for the cohesive failure of the layer and the pouch will comprise transverse fin seals and a longitudinal easy openable lap seal. Examples of blend of polymers exhibiting
5 cohesive failure are for instance those blends of an ethylene terpolymer with an ionomer described in US-A-4,469,754; or of an ethylene polymer and a propylene polymer described in US-A-5,160,767; or those ternary blends of copolymers of acrylic acid or methacrylic acid, modified ethylene vinyl acetate, and polybutylene described in International patent application PCT/EP99/02411; and the like blends.

10 Or, still alternatively, when an easy opening pouch is desired, the outer layer d) may have the same composition of the heat-sealing layer b) but its thickness be less than 10 μm and an intermediate layer e), containing a cohesive failure blend be directly adhered thereto.

When the film of the present invention is employed in the manufacture of bags or
15 pouches, e.g. by folding the flat film and transverse sealing it, a thicker structure (from about 20 to about 80 μm) will be preferred and the outer layer d) will be suitably selected, independently from the outer heat-sealing layer b), with the aim at providing the bag with a high abuse resistance. In such a case preferred resins for said outer layer d) would be polyamides, polyesters, and some polyolefins, such as the heterogeneous
20 or homogeneous ethylene-(C₄-C₈)- α -olefin *co*-polymers having a density from about 0.915 g/cm³ to about 0.935 g/cm³ possibly blended with polyethylene *homo*-polymers, ethylene-vinyl acetate *co*-polymers or ethylene-alkyl (meth)acrylate *co*-polymers; and ethylene-propylene *co*-polymers.

The use of polyamides and polyesters in the outer layer d) is advantageous also for
25 other reasons including printability of the film, stack sealability of the bags/pouches made therewith, resistance to UV radiations, and the like.

Also between the *co*-polyamide layer a) and the outer layer d) it may be necessary or advisable to position a tie layer c'). Tie layer c') is defined as tie layer c) above, but it can be equal or different from c).

In a most preferred embodiment of the present invention, the film will therefore
5 comprise at least 5 layers with tie layers c) and c') positioned between the internal *co*-polyamide layer a) and the outer layers b) and d).

Additional layers may be present in the overall structure to improve the characteristics thereof.

The thermoplastic resins which are employed in these optional, additional, layers
10 need however to be highly orientable at temperatures compatible with the rest of the structure and with the mechanical properties desired for the end film.

Suitable resins are, for example, polyolefins, and in particular heterogeneous ethylene- α -olefin *co*-polymers, homogeneous ethylene- α -olefin *co*-polymers, ethylene-vinyl acetate *co*-polymers, ethylene-(meth)acrylic acid *co*-polymers, ethylene-
15 alkyl(meth)acrylate *co*-polymers, ionomers, propylene polymers, modified polyolefins, and blends thereof. These resins can be used for instance in internal layers to provide the required bulk.

PVDC also is a suitable resin that can be employed in a core layer when high barrier properties (oxygen permeability lower than $50 \text{ cm}^3/\text{m}^2 \cdot \text{day} \cdot \text{bar}$, at 23°C and 0 % or 100
20 % relative humidity) are required.

The resins used in the manufacture of the films according to the present invention can be suitably additivated as known in the art in order to improve the properties of the film or to ease the manufacture thereof.

As an example the resins may contain stabilizers, anti oxidants, pigments, UV
25 absorbers, cross-linking enhancers or cross-linking inhibitors, anti-fog agents or compositions, slip and anti-blocking agents, etc., as conventionally used in this field.

In particular the outer layers may comprise slip and anti-blocking agents as conventionally used in this field, such as silica, either natural or synthetic silica, calcium stearate, amides or bis-amides, etc. They may also contain small amounts of fluorinated hydrocarbon resins to improve processability and in particular improve
5 extrudability and resin distribution through the flat extrusion die.

The thickness ratio between the different layers in the final film is not critical and depends on the overall thickness desired for the end film, on the number of layers in the structure and on the OTR desired for the structure.

The film according to the present invention is manufactured by extrusion of a thick
10 primary tape that is then stretched, either sequentially or simultaneously, using a tenter frame.

The primary tape can be obtained by any known extrusion technique and, if a round die is employed, by opening of the tubular tape to give the sheet to be flat stretched.

However, while hot blown as well as cast extrusion through a round die can be
15 employed, preferably the primary tape is extruded through a flat die.

Preferably the tape is co-extruded but the technique of extrusion coating for the preparation of said primary tape is however possible.

Thus in a preferred embodiment the flat multi-layer tape is extruded onto a cooled roll and quenched as known in the art. Then it is re-heated and stretched in the machine
20 direction and in the transverse direction.

As indicated above the orientation in the machine direction and that in the transverse direction can be carried out separately, wherein, preferably, that in the machine direction is carried out first.

To stretch in the machine direction, the tape is passed through at least two sets of
25 heated rolls revolving at different speed, with the downstream set moving at a higher speed. The temperature at which stretching in the machine direction is carried out typically ranges from about 85 °C to about 140 °C. The pre-heating temperature (i.e.

the temperature of the heated rolls through which the tape is passed before the stretching step starts) and the relaxation temperature (i.e. the temperature of the heated rolls through which the tape is passed after the stretching step in machine direction is complete) are generally 10 to 20 °C higher.

- 5 The stretching ratio in the machine direction is at least 3.0:1 but higher stretching ratios, up to 5.0:1, 6.0:1 or 7.0:1, can be applied.

The stretching in the transverse direction is carried out by means of a tenter frame oven that comprises a certain number of heating zones and suitable stretching means.

- 10 The stretching temperature is typically comprised between about 120 and about 150 °C, with a pre-heating temperature of 5 to 15 °C higher.

The stretching ratio in the transverse direction is at least 6.0:1 but higher stretching ratios, e.g. up to 8.0:1, 9.0:1 or even more, might possibly be applied.

- 15 The transversal orientation is then followed by a heat-setting step that is carried out by subjecting the film, while still clipped but no longer stretched, to a temperature comparable to that used for the transversal stretching. Preferably the stretching rails in the end section of the tenter frame are not kept parallel but are allowed to slightly converge.

- 20 Alternatively the stretching can be carried out simultaneously in both perpendicular directions. This simultaneous stretching is preferably obtained by a system where the clips are propelled throughout the opposed loops of the tenter frame by means of a linear synchronous motor. A suitable line for simultaneous stretching with linear motor technology has been designed by Brueckner GmbH and advertised as LISIM® line.

- 25 In the simultaneous stretching the orientation temperature is typically comprised between about 120 and about 150 °C, with a pre-heating temperature of 5 to 15 °C higher and a heat-setting temperature close to the orientation one.

The film of the present invention may be partially or wholly cross-linked. To produce cross-linking an extrudate is treated with a suitable radiation dosage of high-

energy electrons, preferably using an electron accelerator, with the dosage level being determined by standard dosimetry methods. Other accelerators such as a Van der Graaf generator or resonating transformer may be used. The radiation is not limited to electrons from an accelerator since any ionizing radiation may be used. Radiation dosages are referred to herein in terms of kGreys. A suitable radiation dosage of high energy electrons is up to about 140 kGreys, typically in the range of from about 10 to about 120 kGreys, preferably it is in the range of from about 20 to about 100 and even more preferably in the range of from about 30 to about 80 kGreys.

Irradiation is most preferably performed prior to orientation but it could also be performed during and/or after orientation.

The film may also be printed. In the simplest cases just black letters with the product identification and the instructions for correct product storage or use, or in the most complex cases designs made with various colors, advertising the product and the producer. To improve print adhesion, the film of the present invention may be primed using a coating of a resin that improves adhesion, gloss or durability of the following print, or alternatively the surface of the film which will be printed, can be rendered more receptive to ink by subjecting it to a corona discharge treatment or to any other treatment that is known to increase surface energy, such as flame treatment.

The invention will now be described with reference to the following examples that are intended to be illustrative of some preferred embodiments of thermoplastic films.

Said examples should not be interpreted as a limitation to the scope of the present invention.

Melt Flow Indexes (MFI's), unless otherwise indicated, are measured by ASTM D-1238, Condition E, 190°C/2.16 kg, and are anyway reported in grams/10 minutes.

The densities have been measured by ASTM D 792.

Unless otherwise specifically indicated, all percentages are by weight.

Melting points, if not otherwise indicated, have been determined by DSC following ASTM D-3418 (2nd heating - 10°C/min).

Glass transition points have also been determined by DSC following ASTM D-3418.

5 Example 1

A 5-layer film having the following structure:

A/B/C/B/A, wherein

A is a blend of 49 % of linear low density polyethylene with $d = 0.920 \text{ g/cm}^3$, and MFI = 1 g/10' (Dowlex™ 2045E commercially available from Dow), 24 % of ethylene-vinyl acetate co-polymer with 4.5 % VA, MFI = 2.0 g/10' (Escorene™ LD362BW commercially available from Exxon), 24 % of linear medium density polyethylene with $d = 0.935 \text{ g/cm}^3$, and MFI = 2.6 g/10' (Dowlex™ SC 2102.00 commercially available from Dow), comprising about 0.1 % of silica and about 0.3 % of erucamide, and 3 % of a masterbatch based on LDPE containing fluorinated hydrocarbon resins as processing aids (Sarmawax™ LLT commercially available from Clariant);

B is a modified very low density linear polyethylene (Admer™ AT1094E commercially available from Mitsui); and

C is a multi-polyamide obtained from the following monomers :
20 hexamethylenediamine, meta-xylylenediamine, adipic acid and sebacic acid characterized by a glass transition point of 57 °C and a melting point of 181 °C (Grilon™ XE3569 commercially available from EMS),

and the thickness of the various layers is respectively 12/4/3.5/4/12 µm,

is prepared by co-extrusion through a flat die at a die temperature of about 230 °C.

25 The tape, 920 µm thick and 575 mm wide, is cooled by means of a chill roll kept at 20 °C. The linear speed of the quenched tape is 20 m/min. The tape is cross-linked to 60 kGreys and then pre-heated to a temperature of about 110 °C on oil heated rolls and

stretched in machine direction at a temperature of about 90 °C with a stretching ratio of about 4.0:1. The MD oriented tape is passed through another set of rolls heated to a temperature of about 110 °C for relaxation, and then transferred to a tenter frame oven having four heating zones in which the temperature (pre-heating temperature) is about 135 °C. Stretching, to a TD stretching ratio of about 6.5 : 1, is then carried out at a temperature of about 125 °C, and finally heat-setting is carried out at a temperature of from about 125 °C to about 130 °C.

Finally the film is cooled and wound onto a roll. The obtained biaxially oriented film has a final thickness of about 35 µm.

10 Example 2

A 5-layer film having the following structure:

A/B/C'/B/A, wherein A and B are as in Example 1 and C' is an MXD6/MXDI *co*-polyamide characterized by a glass transition point of 96 °C and a melting point of 213 °C (Grilon™ FE4581 commercially available from EMS),

15 is prepared by following essentially the same procedure as in the foregoing example.

The thickness of the various layers is respectively 7.5/3.5/3.0/3.5/7.5 µm for a total thickness of 25 µm.

Example 3

A 5-layer film having the following structure:

20 A/B/C''/B/A, wherein A and B are as in Example 1 and C'' is a blend of 60 % by weight of a *co*-polyamide 6/12 characterized by a glass transition point of 25 °C and a melting point of 130 °C (Grilon™ CF6S commercially available from EMS), and 40 % by weight of ethylene-vinyl alcohol copolymer with 44 % by mole of ethylene (EVAL EP-E151B commercially available from Kuraray),

25 is prepared by following essentially the same procedure as in example 1.

Example 4

A 5-layer film having the following structure:

A'/B/C'/B/A', wherein

A' is a blend of 87.5 % of an ethylene-propylene-butene terpolymer with $d = 0.899 \text{ g/cm}^3$, and MFI = 5.5 g/10' (ASTM D-1238 at 230 °C and 2.16 kg) (Adsyl™ 5C 37F commercially available from Montell), and 12.5 % of polypropylene homopolymer, with $d = 0.904 \text{ g/cm}^3$, and MFI = 3.0 g/10' (ASTM D-1238 at 230 °C and 2.16 kg) (Profax™ PD064 commercially available from Montell), comprising about 0.1 % of silica and about 0.3% of erucamide;

B is as in Example 1 and C' is as in Example 2

and the thickness of the various layers is respectively 10/4/3.5/4/10 μm , is prepared by co-extrusion through a flat die at a die temperature of about 230 °C and simultaneous stretching (MD 4.0:1, TD 7.0:1).

The temperature in the preheating zone is kept between about 130 °C and about 140 °C and the orientation temperature is comprised between about 120 °C and about 130 °C. Heat-setting is carried out at a temperature of about 130 °C.

Example 5

A 5-layer film having the following structure :

A''/B/A''/B/C'''

wherein A'' is a linear low density polyethylene with $d = 0.920 \text{ g/cm}^3$ (Dowlex™ 2045E commercially available from Dow), B is as in Example 1, and C''' is an MXD6/MXDI *co*-polyamide characterized by a glass transition temperature of 96 °C and a melting temperature of 213 °C, additivated with magnesium stearate, (Grilon™ FE5299 commercially available from EMS), and the thickness of the various layers is respectively 5/3/12/3/12 μm , is prepared by co-extrusion through a flat die equipped with a deckling system, at a die temperature of about 230 °C, irradiation of the obtained tape at about 100 kGy, followed by simultaneous stretching (with stretching ratio in the machine direction of 4.0:1 and stretching ratio in the transverse direction of 7.0:1) at an orientation temperature comprised between 120 and 130 °C (pre-heating at 130-140 °C) and finally by heat-setting at about 130 °C.

Example 6

A 5-layer film having the following structure :

$$A'''/B/A'''/B/C'''$$

wherein A''' is an ethylene-propylene copolymer (Moplen™ EP2C30F commercially available from Montell), B is as in Example 1, and C''' is as in Example 5, and the thickness of the various layers is respectively 4/3/10/3/10 μm, is prepared by co-extrusion through a flat die equipped with a deckling system, at a die temperature of about 250 °C, irradiation of the obtained tape at about 75 kGy, followed by simultaneous stretching (with stretching ratio in the machine direction of 4.0:1 and stretching ratio in the transverse direction of 6.0:1) at an orientation temperature comprised between 130 and 140 °C (pre-heating at 140-150 °C) and finally by heat-setting at about 150 °C.

Example 7

A 7-layer film having the following structure :

$$A''/B'/A'''/B'/C'''/B'/D$$

wherein A'' and C''' are as in Example 5, A''' is as in Example 6, B' is a rubber modified ethylene-α-olefin copolymer grafted with maleic anhydride (Admer™ 1335 E commercially available from Mitsui), and D is a polypropylene homopolymer with $d = 0.905 \text{ g/cm}^3$ and MFI of 3.0 g/10 min (at 230 °C and 2.16 kg) (Polypropylene KF6100 commercially available from Montell), and the thickness of the various layers is respectively 10/5/15/5/5/5/10 μm, is prepared by co-extrusion through a flat die, at a die temperature of about 250 °C, irradiation of the obtained tape at about 100 kGy, followed by stretching in the machine direction at a stretching temperature of about 90 °C (preheating at about 95 °C) and with a stretching ratio of 5.0:1 and in the transverse direction at a stretching temperature of about 140 °C (pre-heating at about 150 °C) and with a stretching ratio of 7.0:1, finally followed by heat-setting at about 140 °C.

Example 8

A 7-layer film having the following structure :

$$A''/B'/A'''/B'/C'''/B'/D'$$

wherein A'' and C''' are as in Example 5, A''' is as in Example 6, B' is as in Example 7, and D' is a co-polyester based on polyethyleneterephthalate units and containing 1,4-cyclohexanediol co-monomers (PETg – Eastman 6763 commercially available from Eastman Chemicals), and the thickness of the various layers is respectively
5 10/5/15/5/5/5/10 μm ,

is prepared by co-extrusion through a flat die, at a die temperature of about 250 °C, irradiation of the obtained tape at about 100 kGy, followed by stretching in the machine direction at a stretching temperature of about 85 °C (preheating at about 90 °C) and with a stretching ratio of 4.0:1 and in the transverse direction at a stretching
10 temperature of about 135 °C (pre-heating at about 145 °C) and with a stretching ratio of 6.5:1, finally followed by heat-setting at about 140 °C.

The properties of representative films of the present invention have been evaluated by submitting the films to the tests indicated below.

% Free shrink : the percent free shrink, i.e. the irreversible and rapid reduction, as a
15 percent, of the original dimensions of a sample subjected to a given temperature under conditions where nil restraint to inhibit shrinkage is present, has been measured according to ASTM D2732, by immersing for 4 seconds specimens of the structures to be tested (10 cm x 10 cm) into a bath of hot oil at 100 °C. This attribute has been measured in the machine or longitudinal direction (MD) as well as in the transversal
20 direction (TD) and is reported as the sum thereof, i.e. the total free shrink.

Oxygen Transmission rate (OTR) : OTR is evaluated, at 23 °C and 0 % R.H., according to ASTM D-3985 using an OX-TRAN instrument by Mocon and is expressed as $\text{cm}^3/\text{m}^2.\text{day}.\text{bar}$.

Haze : haze is defined as that percentage of transmitted light which in passing
25 through the specimen deviates from the incident beam by forward scattering, and it has been measured by ASTM D 1003 (Procedure A).

Gloss : the specular gloss of the films, i.e. the relative luminous reflectance factor of a specimen in the mirror direction has been measured using ASTM 2457 - 90 with a gloss angle of 60°.

Modulus : the ratio of the tensile stress to corresponding strain below the proportional limit (kg/cm²); measured by ASTM D 882.

Tensile : a measure of the force required at constant elongation to break a specimen of the film (kg/cm²); measured by ASTM D 882.

Elongation : a measure of the percent extension required to break a specimen of the film (%); measured by ASTM D 882.

Thickness variation % : is the percent value obtained by measuring the maximum and minimum thickness of the film, calculating the average thickness value and applying these numbers to the following formula:

$$\text{Thickness variation (\%)} = \frac{\text{film thickness}_{(\max)} - \text{film thickness}_{(\min)}}{\text{film thickness}_{(\text{avg})}} \times 100.$$

The maximum and minimum thicknesses are determined by taking a total of 10 thickness measurements at regular distance intervals along the entirety of the transverse direction of a film sample, recording the highest and lowest thickness values as the maximum and minimum thickness values, respectively, while the average value is determined by summing up the same 10 thickness measurements and dividing the result by ten. The thickness variation is then computed (as a percent value) using the formula above. A thickness variation of 0 % represents a film with no measurable differences in thickness. A thickness variation over 20 % is unacceptable industrially while a thickness variation below 10 % is a good value.

Puncture resistance : the puncture resistance is the resistance force arising when pushing a punch against a surface of flexible film. There is not a standard test method to measure this attribute. The test method used in the present evaluations is described

briefly herein below : a film sample (6.5 cm x 6.5 cm) is fixed in a specimen holder connected to a compression cell (1-50 kg normal sensitivity) mounted on a dynamometer (an Instron tensile tester); when the dynamometer is started, a punch (a punching sphere, 5-mm in diameter, soldered on a plunger) is brought against the film sample at a constant speed (30 cm/min.) and the force needed to puncture the sample is graphically recorded.

The % Shrink, OTR, Haze, Gloss, Modulus, Tensile, Elongation, and % Thickness Variation of some representative structures of the present invention are reported in Table 1 below

TABLE 1

Structure of			
Example no.		1	2
15	% Shrink at 100 °C		
	MD	1	2
	TD	2	3
	OTR	-	86
	Haze	4.	2.5
20	Gloss	110	128
	Modulus		
	MD	5850	5930
	TD	5120	5240
	Tensile		
25	MD	430	470
	TD	660	740
	Elongation		

MD	220	280
TD	120	130
% Thickness variation	3	2

The results of the Puncture resistance test for a representative film of the present invention is reported in Table 2 below. More particularly a comparison has been made between the film of Example 2 of the present invention, having a thickness of 25 μm , and a cast coextruded commercial structure currently used as tray lidding, 65 μm thick, containing about 25 wt. % polyamide and about 40 wt. % of propylene based polymers (Comparative Example A) and another cast co-extruded commercial structure used for liquid packaging with VFFS machines, 130 μm thick, containing about 25 wt. % of polyamide and 12 wt. % of ethylene-vinyl alcohol (Comparative Example B).

TABLE 2

	Example 2	Comp. Ex. A	Comp. Ex. B
Puncture (g) 30°C	3,000	1,400	3,100

The film of Example 2 of the present invention has been tested for use as the lidding film in a standard thermoforming Tiromat Powerpack machine under the following packaging conditions: sealing temperature: 120°C and sealing time 2 s, showing good sealability and good machinability.

The same film has been tested also on a VFFS machine for liquid packaging (Onpack® 2050, a machine manufactured by Orihiro) under the following packaging conditions: sealing temperature 140-150 °C, sealing time 0.8 – 1 s, machine speed 20/30 ppm, with good results as for sealability and machinability.

Finally the film of Example 2 has been evaluated also on a Hayssen 1800 RT machine at 90 ppm without any problem.

CLAIMS

1. A multi-layer, thermoplastic film, bi-axially oriented at a stretching ratio \geq about 3.0:1 in the machine direction and at a stretching ratio \geq about 6.0:1 in the transverse direction, which film comprises
5 a layer a) comprising at least 50 wt. % of a crystalline or partially crystalline *co*-polyamide characterized by a $T_g \leq 100^\circ\text{C}$, and at least one outer heat-sealing layer b) comprising a polyolefin, said film being further characterized in that it has a % free shrink at $100^\circ\text{C} \leq 3$ in each direction.
- 10 2. A film as in claim 1 which is bi-axially oriented at a stretching ratio \geq about 3.5:1, preferably \geq about 3.8:1, and more preferably \geq about 4.0:1, in the machine direction and at a stretching ratio \geq about 6.2:1, and preferably \geq about 6.5:1, in the transverse direction.
- 15 3. A film as in claim 1 wherein the crystalline or partially crystalline *co*-polyamide characterized by a $T_g \leq 100^\circ\text{C}$ of layer a) is selected from the group consisting of aliphatic *co*-polymers obtained by *co*-polymerization of ϵ -caprolactam and ω -laurolactam, aliphatic *co*-polymers obtained by *co*-polymerization of ϵ -caprolactam, hexamethylenediamine and azelaic acid, polyamide *co*-polymers obtained from meta-xylylendiamine, adipic acid and isophthalic acid and multi-polyamides obtained from hexamethylenediamine,
20 meta-xylylendiamine, adipic acid, and sebacic acid.
- 25 4. A film as in claim 1 wherein the *co*-polyamide of layer a) is used alone or in admixture with less than about 50 wt. %, preferably less than about 40 wt. %, and even more preferably less than about 30 wt. %, of another resin compatible therewith that does not impair the orientability of the overall structure, such as crystalline or partially crystalline polyamides having a $T_g > 100^\circ\text{C}$, amorphous polyamides, ethylene-vinyl alcohol *co*-polymers, polyesters and *co*-polyesters.

5. The film of claim 1 wherein the polyolefin resin(s) of the outer heat-sealing layer b) has a melting point $< 150^{\circ}\text{C}$, and preferably $< 140^{\circ}\text{C}$.
6. The film of claim 5 wherein the polyolefin resin(s) of the outer heat-sealing layer b) has a melting point comprised between about 80°C and about 135°C and preferably comprised between about 90°C and about 128°C .
7. The film of claim 1 wherein the outer heat-sealing layer b) comprises one or more polymers selected from the group consisting of heterogeneous or homogeneous ethylene- ($\text{C}_4\text{-C}_8$)- α -olefin *co*-polymers having a density $\leq 0.925\text{ g/cm}^3$; blends thereof with minor amount of polyethylene *homo*-polymers or heterogeneous or homogeneous ethylene- ($\text{C}_4\text{-C}_8$)- α -olefin *co*-polymers having a density $> 0.925\text{ g/cm}^3$; ethylene-vinyl acetate *co*-polymers; ethylene-acrylic or methacrylic acid *co*-polymers including ionomers; blends of heterogeneous or homogeneous ethylene- ($\text{C}_4\text{-C}_8$)- α -olefin *co*-polymers having a density from about 0.915 g/cm^3 to about 0.935 g/cm^3 with ethylene-vinyl acetate *co*-polymers or ethylene-alkyl (meth)acrylate *co*-polymers; ethylene-propylene-*co*-polymers; ethylene-propylene-butene *ter*-polymers; and ethylene-alkyl acrylate-maleic anhydride *ter*-polymers.
8. A film as in claim 1 wherein a tie layer c) is positioned between the layer comprising the *co*-polyamide a) and the outer heat-sealing polyolefin layer b) wherein said tie layer will comprise a modified ethylene- α -olefin *co*-polymer or a modified *co*-polymer of ethylene and an ethylenically unsaturated ester.
9. A film as in claim 1 wherein the *co*-polyamide layer a) is an internal layer and the film have an additional outer layer d).
10. The film of claim 9 wherein said outer layer d) comprises polyolefins, polyamides, or polyesters.
11. The film of claim 10 wherein the outer layer d) comprises one or more polyolefins.

12. The film of claim 9 which comprises five layers wherein tie layers c) and c') are positioned between the internal co-polyamide layer a) and the outer layers b) and d) respectively.
13. The film of claim 1 which is coextruded.
- 5 14. The film of claim 1 which is irradiated.
15. A process of manufacture of a film as in claim 1 which process comprises stretching an extruded tape comprising
a layer a) comprising at least 50 wt. % of a crystalline or partially crystalline co-polyamide characterized by a $T_g \leq 100$ °C, and
10 at least one outer heat-sealing layer b) comprising a polyolefin,
in the machine direction with a stretching ratio of $\geq 3.0:1$ and in the transverse direction with a stretching ratio of $\geq 6.0:1$, either sequentially or simultaneously, at suitably selected orientation temperatures and then heat-setting the film at a temperature from about 15 °C below the orientation
15 temperature applied to the same orientation temperature or even higher.
16. The process of claim 15 wherein the extruded tape is irradiated.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/02229

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/08 B32B27/34 B29C55/12 B29C47/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 967 073 A (KUREHA CHEMICAL IND CO LTD) 29 December 1999 (1999-12-29) page 2, line 24 -page 5, line 24 page 6, line 43 - line 23 page 9, line 15 -page 10, line 26; examples 1-5; table 1 claims 1-8	1-13
Y	EP 0 465 931 A (GUNZE KK) 15 January 1992 (1992-01-15) page 3, line 18 -page 4, line 4 page 5, line 32 -page 6, line 20 page 9, line 29 -page 10, line 20; table 2 -/--	1-13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/02229

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 288 972 A (MITSUBISHI GAS CHEMICAL CO) 2 November 1988 (1988-11-02) page 2, line 44 -page 4, line 17 page 5, line 4 - line 23 page 7, line 43 -page 8, line 4; table 1 claims 1-4 ----	1-4,9-14
A	EP 0 719 631 A (TOYO BOSEKI) 3 July 1996 (1996-07-03) page 3, line 9 - line 57 page 5, line 29 - line 40 page 7, line 32 -page 8, line 19; table 1 ----	1-4,15
A	EP 0 685 510 A (UNITIKA LTD) 6 December 1995 (1995-12-06) page 4, line 46 -page 5, line 2 page 7; table 1 page 10; examples 1-11; table 3 claims 1-8 ----	1-4,15
A	EP 0 358 038 A (VISKASE CORP) 14 March 1990 (1990-03-14) page 5, line 17 -page 8, line 50 page 12, line 37 -page 13, line 38; table 5 -----	1-13
A	page 15, line 31 - line 37 -----	15,16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/02229

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0967073 A	29-12-1999	JP 2000079669 A	21-03-2000
EP 0465931 A	15-01-1992	JP 2997814 B	11-01-2000
		JP 4059244 A	26-02-1992
		JP 3028341 B	04-04-2000
		JP 4185322 A	02-07-1992
		AU 643035 B	04-11-1993
		AU 7929991 A	02-01-1992
		DE 69119982 D	11-07-1996
		DE 69119982 T	24-10-1996
		ES 2087179 T	16-07-1996
		NZ 238706 A	22-12-1994
		US 5562996 A	08-10-1996
		US 5688456 A	18-11-1997
EP 0288972 A	02-11-1988	JP 2069502 C	10-07-1996
		JP 7102658 B	08-11-1995
		JP 63267548 A	04-11-1988
		JP 2069503 C	10-07-1996
		JP 7102659 B	08-11-1995
		JP 63267549 A	04-11-1988
		AU 604896 B	03-01-1991
		AU 1638588 A	23-11-1989
		CA 1279811 A	05-02-1991
		DE 3884042 D	21-10-1993
		DE 3884042 T	03-02-1994
		US 4908272 A	13-03-1990
EP 0719631 A	03-07-1996	JP 8174663 A	09-07-1996
		CN 1133235 A	16-10-1996
		EP 0927624 A	07-07-1999
		US 5718965 A	17-02-1998
		US 5968665 A	19-10-1999
EP 0685510 A	06-12-1995	JP 8047972 A	20-02-1996
		DE 69501288 D	05-02-1998
		DE 69501288 T	14-05-1998
		US 5612105 A	18-03-1997
EP 0358038 A	14-03-1990	US 5053259 A	01-10-1991
		AT 122370 T	15-05-1995
		DE 68922554 D	14-06-1995
		DE 68922554 T	29-02-1996
		US 5480945 A	02-01-1996
		US 5344679 A	06-09-1994

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